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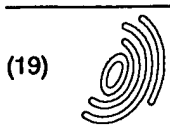
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(54) Coating composition with improved adhesion on chalky substrates

Beschichtungsmittelzusammensetzung mit erhöhter Haftung auf gekreidetem Untergrund

Composition de revêtement et méthode pour l'adhésion améliorée aux substrates crayeux

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(56) References cited:
• PATENT ABSTRACTS OF JAPAN vol. 15 no. 216
(C-837) & JP-A-03 064305 (ASAHI CHEM IND CO
LTD)

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EP 0 658 608 B1

Description

[0001] The present invention relates to a composition and a method for improving adhesion of coatings to chalky substrates.

[0002] Water-based latex paints have found wide use and acceptance in exterior applications. Water-based latex paints have proven their exterior durability and toughness and, because they are water-based, health, safety and environmental concerns are significantly minimized relative to solvent-based alkyd paints. However, water-based latex paints have inferior adhesion over difficult surfaces such as "chalky substrates" when compared to solvent-based alkyd paints.

[0003] Chalky substrates result when the latex paint degrades from exposure to rain and sunlight. The degradation process causes pigments and extenders, such as titanium dioxide and aluminium silicates, to become unbound and to appear on the painted surface as a dusty white chalk. Solvent-based alkyd paints continue to out-perform water-based latex paints over these substrates because of their ability to wet, penetrate and adhere to chalky substrates.

[0004] JP 03-064305A discloses an aqueous silane-modified macromolecular dispersion composition for improving the wet adhesion of adhesives and paints to glass which consists of a carboxyl group-containing water-soluble resin, a macromolecular aqueous dispersion and a water-soluble silane coupling agent containing an amino group. The carboxyl group-containing water-soluble resin has an acid number of 30-800 and the amount compounded are per 100 solid parts by weight of the macromolecular aqueous dispersion, 0.2 to 2.0 parts by weight of the water-soluble resin and 0.1 to 3.0 parts by weight of the amino group-containing silane coupling agent.

[0005] US-A-4,340,524 discloses an acrylic resin latex-based sealant composition with improved water resistance and wet adhesion to glass and aluminium which comprises introducing about 0.1 to about 10 weight percent of a hydrophobic resin dissolved in about 2 to about 20 weight percent of a liquid organic, non-coagulating, non-gelling solvent into the acrylic resin latex together with an aqueous solution of about 0.5 to about 5.0 weight percent of a hydrolyzed organoaminosilane containing sufficient base to maintain a pH of at least 8.5.

[0006] PCT WO 92/14788 discloses a composition that provides quasi-crosslinked, alkali-soluble polymeric surface coatings which includes an acid-functional vinyl polymer and an amino-functional siloxane, in which the vinyl polymer has at least two acid-functional pendant moieties and in which the siloxane polymer has at least two amino-functional pendant moieties.

[0007] US-A-5,202,378 discloses a polymeric binder exhibiting excellent chalk adhesion to which the protective coating composition contains a film-forming polymeric binder comprising emulsion copolymerized ethylenically unsaturated monomers including minor amounts of a fatty acid methacrylate or acrylate.

[0008] Another way well known in the art to obtain chalk adhesion of latex paints is to blend a solvent-based alkyd into a latex paint. Although this type of blend improves chalk adhesion of the latex paint, the solvent-based alkyd causes undesirable oxidative degradation of the paint film. Various patents including US-A-4,504,609, US-A-4,529,765, US-A-4,199,400 and US-A-3,454,516, demonstrate the blending of a solvent-based alkyd with a latex for improved chalk adhesion properties.

[0009] The present invention aims to improve adhesion of coatings to chalky substrates.

[0010] One aspect of the invention provides a composition for improving adhesion of a coating to a chalky substrate, comprising a blend of a macromolecular aqueous dispersion latex, an acid-functional alkali-soluble resin and an aminosilane.

[0011] In another aspect of the invention there is provided a method for improving adhesion of a coating to chalky substrates, the method comprises adding the composition to the coating and applying the coating to the chalky substrate.

[0012] Some of the major advantages of the present invention are that: it minimizes safety, health and environmental concerns by being water-based; it allows for the substitution of a water-based latex paint in the market that was previously dominated by solvent-based alkyd paints; and the use of the water-based latex system of the present invention over chalky substrates is possible without compromising physical properties such as adhesion.

[0013] The inventors have found that the composition of the present invention may be used as a binder for a coating to improve adhesion of the coating to chalky substrates.

Macromolecular Aqueous Dispersion

[0014] The macromolecular aqueous dispersion, also known as a latex or emulsion polymer, used in this invention can be any one of many used in architectural coatings-type applications. Suitable monomers for the preparation of polymers to be used in the macromolecular aqueous dispersion according to the invention are olefinically unsaturated compounds which are also employed for the preparation of conventional paint dispersions, such as: esters of acrylic acid or methacrylic acid with alcohols from 1 to 8 carbons, such as, but not limited to, ethyl acrylate, n-butyl acrylate, isobutyl acrylate, 2-ethylhexyl acrylate, methyl methacrylate, butyl methacrylate; vinyl esters such as, but not limited to,

vinyl acetate, vinyl propionate, vinyl isobutyrate, vinyl esters of 2-ethyl hexanoic acid, vinyl esters of branched C-9 or C-10 carboxylic acids; monovinyl aromatic compounds such as, but not limited to, styrene and vinyl toluene, vinyl chloride, vinylidene chloride, acrylonitrile and ethylene. Minor amounts of unsaturated monocarboxylic acid, their amides or nitriles such as acrylic acid, methacrylic acid, itaconic acid, maleic acid, fumaric acid, acrylamide and methacrylamide
 5 can be included. Also included may be a variety of functional monomers in minor amounts including hydroxyethyl acrylate, hydroxyethyl methacrylate, hydroxypropyl acrylate, hydroxypropyl methacrylate, sodium vinyl sulfonate, sodium styrene sulfonate, sulfoethyl methacrylate and acetoacetoxyethyl methacrylate and many others including adhesion promoting monomers, such as disclosed and prepared in accordance with US-A-2,980,652; 4,599,417 and 4,777,265.

[0015] Preferred monomers are those which produce stable dispersions. The quantitative ratios must be selected according to practices well known in the art in such a way that polymers are made having minimum film formation temperatures below or within the range of the intended application temperatures and having desired degree of flexibility and rigidity.

[0016] Particle size of these macromolecular aqueous dispersions can be in the range from 0.05 to 1.0 micron. Also included are various particle size distributions prepared by either blending or in-situ polymerization. Macromolecular aqueous dispersions can be prepared by polymerization of polymer particles of different sizes, where several distinct maxima in the particle size distribution creates a polymodal dispersion and where two such distinct maxima in the particle size distribution curve creates bimodal dispersions. The preparation of bimodal dispersion is further described in US-A-4,384,056. Also, non-spherical particles such as multilobal particles can be prepared as disclosed in US-A-4,791,151.

[0017] Polymerizations are carried out using typical ionic and/or non-ionic emulsifiers, initiators, and polymerization conditions (+10° C to +100° C).

[0018] Depending on the type of monomers used, at the end of the polymerization, the dispersions are adjusted to a pH ranging from about 5 to about 10, preferably from about 7 to about 9, by means of alkali, ammonia or amines.

25 Alkali-Soluble Resins

[0019] The acid-functional alkali-soluble resin to be neutralized with the aminosilane in accordance with the present invention can be prepared via any processes known in the art. The low molecular weight acid-functional alkalisoluble resin with a weight average molecular weight of less than about 100,000 can be prepared via any emulsion or solution
 30 polymerization process that can be used to produce as such an acid-functional alkali-soluble resin which is water dispersible. Suitable monomers for the preparation of alkalisoluble resins according to the invention are olefinically unsaturated compounds such as: esters of acrylic acid or methacrylic acid with alcohols from 1 to 8 carbons, such as, but not limited to, ethyl acrylate, n-butyl acrylate, isobutyl acrylate, 2-ethyl hexyl acrylate, methyl methacrylate and butyl methacrylate; vinyl esters such as, but not limited to, vinyl acetate, vinyl propionate, vinyl isobutyrate, vinyl esters of 2-ethyl
 35 hexanoic acid and vinyl esters of branched C-9 or C-10 carboxylic acids; monovinyl aromatic compounds such as, but not limited to, styrene and vinyl toluene; vinyl chloride, vinylidene chloride and ethylene. Preferably, the alkali-soluble resin may contain from about 0 weight percent to about 90 weight percent of ethyl acrylate, butyl acrylate, methyl methacrylate and/or styrene based on total weight of the polymer.

[0020] Acid functionality is usually, but not in all instances, limited to the use of acid-functional monomers, such as, for example, acrylic acid, methacrylic acid fumaric acid, maleic acid, crotonic acid, itaconic acid, sodium styrene sulfonate, sulfoethyl methacrylate, acrylamidopropansulphonic acid, and vinylsulphonic acid. Preferably, acrylic acid and/or methacrylic acid and/or itaconic acid are used as monomer units containing acid groups in the practice of this invention at levels from about 50 weight percent to about 5 weight percent. The acid level of the alkali-soluble resin should be at the indicated levels to ensure solubility upon addition of the aminosilane. If the acid level is below the levels indicated, adhesion over chalky substrates is compromised. preferably, the alkali-soluble resin contains from about 70
 45 to about 90 weight percent ethyl acrylate and from about 10 to about 30 weight percent methacrylic acid based on total weight of the polymer.

[0021] To obtain appropriate molecular weight alkali-soluble resins with a weight average molecular weight of less than about 100,000 and to ensure their solubility, chain transfer agents are added to the polymerization in levels from 0.5 weight percent to 10 weight percent based on the total weight of monomers. Such chain transfer agents may be selected from, but are not limited to, the group consisting of n-dodecyl mercaptan, t-dodecyl mercaptan, methyl mercaptopropionate, butyl mercaptopropionate and 3-mercaptopropionic acid, as well as others known to those skilled in the art. Alternate routes to low molecular weight alkali-soluble resins with a weight average molecular weight of less than about 100,000, including high temperature solution polymerizations, are also appropriate.

[0022] Also included may be a variety of functional monomers in minor amounts including hydroxyethyl acrylate, hydroxyethyl methacrylate, hydroxypropyl acrylate, hydroxypropyl methacrylate, sodium vinyl sulfonate, sodium styrene sulfonate, sulfoethyl methacrylate, acetoacetoxyethyl methacrylate, and many others including adhesion promoting monomers, such as disclosed and prepared in accordance with US-A- 2,980,652; 4,599,417 and 4,777,265.

[0023] Polymerizations are carried out using typical ionic and/or non-ionic emulsifiers, initiators, and polymerization conditions (+10° C to +100° C) known to those skilled in the art.

[0024] In this invention, the acid-functional alkali-soluble resin is blended with the macromolecular aqueous dispersion in levels from about 1 weight percent to about 50 weight percent based on total polymer weight. More preferably, the alkalisoluble resin is blended with the macromolecular aqueous dispersion in levels from about 5 weight percent to about 20 weight percent. In addition, the alkali-soluble resin can be prepared in-situ with the macromolecular aqueous dispersion at similar ratios by a sequential polymerization process as disclosed and prepared in accordance with US-A-4,016,171 and 4,876,313.

10 Aminosilane

[0025] The aminosilane-modified latex of the present invention is prepared by adding an effective amount of an aminosilane to a blend of an acid-functional alkali-soluble resin and a macromolecular aqueous dispersion. The quantity of aminosilane that is added to the polymer is a function of the acid content of the alkali-soluble resin. A sufficient amount of aminosilane is added to neutralize from about 50 percent to about 100 percent of the acid content of the alkali-soluble resin. If an excess of an aminosilane, i.e. greater than or equal to 100 weight percent of that which is needed to neutralize the acid component of the alkali-soluble resin, adhesion to chalky substrates is not compromised.

[0026] In general, aminosilanes are organic materials containing silicone and amine functionality. Aminosilanes found to effectively neutralize alkali-soluble resins to achieve adhesion to chalky substrates may be selected from, but are not limited to, the group consisting of trimethoxysilylpropyldiethylenetriamine (Huls T2910 or A-1130 from Union Carbide), N-methylaminopropyltrimethoxysilane, N-(2-aminoethyl)-3-aminopropylmethyldimethoxysilane (Huls A0699), N-(2-aminoethyl)-3-aminopropyltrimethoxysilane (Dow Corning Z-6020, Huls A0700 or A1120 from Union Carbide), aminopropylmethyldimethoxysilane, 3-aminopropyltrimethoxysilane (Huls A0800 or A1110 from Union Carbide), 3-aminopropylmethyldiethoxysilane (Huls A0742) and methylaminopropyltriethoxysilane (Huls A0750 or A1100 from Union Carbide) are available from Dow Corning, Midland, Michigan, Union Carbide Speciality Chemicals Division, Danbury Connecticut and Huls of America, Piscataway, New, Jersey.

[0027] It is believed that the combination of the aminosilane with an acid-functional alkali-soluble resin aids in the minimization of the water sensitivity of the paint film as well as providing a coupling mechanism for the coating to the chalk. However, this is merely a theory of the present invention and should not be considered in any way whatsoever to limit the scope of such, which is more specifically defined in the claims.

Additives

[0028] The blend of this invention of the macromolecular aqueous dispersion and alkali-soluble resin neutralized with aminosilane, may be formulated into paints or coatings according to the desired end-use. Additives such as thickeners, dispersants, pigments, extenders, fillers, antifreeze agents, plasticizers, coalescents, wetting agents, defoamers, colorants, biocides, soaps and slip agents may be incorporated as per procedures known to those skilled in the art.

TEST METHODS

[0029] Adhesion to chalky substrates is measured in a number of different ways, including Crosshatch Adhesion, Knife Peel Adhesion, as well as Force-to-Peel Adhesion. The substrate is a typical commercial alkyd paint which has been naturally weathered to achieve an ASTM chalk rating of 5. Boards were painted with a commercially acceptable alkyd paint and then exposed to rain and sunlight, causing the polymer to degrade and the formation of unbound pigment and extenders referred to as "chalk". Adhesion is tested over this type of substrate.

[0030] Both crosshatch and knife peel adhesion involve the application of the paints via a brush onto the chalked substrates. Two coats of the test paints are applied on the test area using a spread rate of 450 sq. ft./gallon. The test panels are allowed to dry for 4 to 5 hours in between coats. The test panels are then allowed to dry for 7 days under controlled conditions 21°C (70° F), 50% RH. Following a 7 day dry, the test panels are placed in a fog box (simulating rain conditions) for one hour prior to actual crosshatch and knife peel adhesion testing.

[0031] In the crosshatch adhesion testing, a Gardner Adhesion Knife with a 100 square grid is used to scribe the test area. The area is then patted dry and a piece of tape with a 3.81cm (1.5") overhang to form a pull tab (typically Permaceel 2.54cm (1") tape) is applied over the test area. The tape is rubbed with an eraser to assure good contact over the test area, and then using the overlap for grip, the tape is pulled quickly at a 180° angle from the substrate. The test area is then rated for paint remaining by counting the squares of paint left behind. A rating of 100 is excellent adhesion as none of the test paint was removed by the tape; therefore, implying excellent adhesion between the test paint and the chalked substrate. A rating of 0 is poor adhesion. Through much experience, we believe that obtaining a crosshatch adhesion of at least 50 is significant adhesion.

[0032] Knife peel adhesion requires using an Excel Adhesion Knife (or comparable one) to make two knife cuts forming a X intersecting at about a 30° angle. The point of the Excel Adhesion Knife is then used to attempt to peel the latex paint from the substrate, at the point of intersection. The degree of peeling difficulty is rated subjectively according to the following scale:

5

- 10 = no peeling
- 9 = very difficult
- 8 = difficult
- 7 = moderately difficult
- 10 6 = slightly to mod. difficult
- 5 = slightly difficult
- 4 = fairly easy
- 3 = easy
- 2 = very easy
- 15 1 = falls off

[0033] A knife peel rating of 6 or above is considered significant adhesion.

[0034] Force-to-peel adhesion involves the same chalked substrates, the same drying conditions and the same exposure time in the fog box. Test panel preparation involves applying 2.5 grams of test paint to a 5.08cm x 15.24cm (2" X 6") area of the substrate; immediately placing a 3.81cm x 22.86cm (1.5" X 9") strip of cheesecloth on the wet paint, leaving a 3.81cm (1.5") overhang over the edge; firmly pressing the cheesecloth into the wet paints, and then saturating the cheesecloth by applying an additional 5.5 grams of test paint. After drying for 7 days at controlled conditions 21°C (70° F), 50% RH, a 2.54cm (1") wide strip is cut through the length of the cheesecloth using a utility knife and a template. The test panel is then placed in a fog box for one hour. After removing the panel from the fog box, it is attached horizontally to a ring stand slanting forward at approximately 10° from the perpendicular using utility/burette clamps. The thin edge of the test panel must be in the up direction. A weight hanger is attached to the cheesecloth via an S hook or paperclip. Weight is then increased on the hanger in 10, 20 and 50 gram increments until the cheesecloth peels away from the substrate at a rate of 10-20 mm/minute. The panel may be marked with a scale or rule to use as a guide for determining the rate of separation. The untested areas must be kept wet during the testing by draping them with a water-saturated piece of cheesecloth.

[0035] The amount of weight in grams required to achieve the separation, up to 1500 grams, is reported as well as the mode of failure:

- Cohesive: Failure of paint itself, rather than bond between the test paint and the substrate
- 35 Adhesive: Separation of the test paint from the substrate
- Substrate: Total paint failure into the wood surface

[0036] Typically the achievement of from about 800 grams and higher in this test is considered significant adhesion. In addition, any cohesive failure (as opposed to 100% adhesive failure) is indicative of true improvements in adhesion.

40

GLOSSARY

[0037]

- 45 AA = acrylic acid
- ASR = alkali soluble resin
- BA = butyl acrylate
- EA = ethyl acrylate
- MAA = methacrylic acid
- 50 MMA = methyl methacrylate
- MMP = methyl mercaptopropionate
- STY = styrene
- SVS = sodium vinylsulfonate
- VA = vinyl acetate

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[0038] The following examples are provided to further illustrate some of the embodiments of the present invention. They should not be interpreted as limiting the scope of the invention, which is more specifically defined in the claims.

EXAMPLES

[0039] The blends in Table I through Table VI were prepared by adding 80 to 95 weight percent of the macromolecular aqueous dispersion to a container. The pH of this dispersion is measured and designated as the initial pH. Under agitation, supplied by a typical laboratory mixer, the alkali-soluble resin at 20 to 5 weight percent was added. The pH of the system was monitored to ensure that the pH of this mixture does not drop below a value which would jeopardize the stability of the macromolecular aqueous dispersion.

[0040] The aminosilane is then added slowly to this mixture so that all of the acid introduced into the mixture from the alkali-soluble resin is indeed neutralized by the aminosilane. If the pH of the mixture of the macromolecular aqueous dispersion and the alkali-soluble resin begins to drop below the critical pH required for dispersion stability, the alkali-soluble resin may be added in increments, following each increment addition by the addition of some aminosilane until all of the alkali-soluble resin was added and the desired initial pH was obtained.

[0041] The above-prepared blend was then added to a paint in the traditional way known to all of those skilled in the art of paint formulating. In Tables I through Table VI below, data has been reported where the blends are formulated into 45% PVC (Pigment Volume Concentration) and 36% VS (Volume Solids) paints which contained traditional titanium dioxide and extenders used for exterior flat paints.

[0042] Although the present evaluation was limited to exterior flat paints, it is intended that the use of blends of a macromolecular aqueous dispersion, alkali-soluble resin and aminosilane can be used in other formulation types such as, but not limited to, high gloss, semi-gloss, sheen paints as well as primers, to improve their chalk adhesion.

Example 1

[0043] Example 1 demonstrates the use of a blend of a macromolecular aqueous dispersion, alkali-soluble resin and an aminosilane. Comparison to a non-modified macromolecular aqueous dispersion shows improvements in chalk adhesion. In this example, the macromolecular aqueous dispersion is designated as Latex A with the composition of 49 BA/49 MMA/2 MAA and was prepared using the following procedure:

[0044] A 5 liter glass reactor with an agitator, a thermocouple for monitoring the temperature and a reflux condenser, was charged with 800 g of deionized water and purged with nitrogen. After heating to 88° C, 4.0 g of ammonium persulfate dissolved in 20 g of deionized water and 165 g of a seed latex (45% solids, 100 nm diameter) were added to the reactor. The temperature was adjusted to 85° C, and then a pre-emulsion prepared from 980 g butyl acrylate, 980 g methyl methacrylate, 40 g methacrylic acid, 5.0 g sodium dodecylbenzenesulfonate and 517 g deionized water and an additional 3.0 g of ammonium persulfate dissolved in 90 g deionized water were added to the reactor over a three hour time period while maintaining the temperature at 85° C. When the additions were complete, the temperature was maintained at 85° C for an additional 30 minutes. The reaction was cooled to 60° C and 4 g of t-butyl hydroperoxide dissolved in 20 g of deionized water and 3 g of sodium formaldehydesulfoxylate dissolved in 40 g of deionized water were added. The pH was adjusted with 40 g of 14% aqueous ammonia. Then 57.4 g of Triton X-405 surfactant dissolved in a equal weight of deionized water was added. The resulting latex had a solids content of 54.7%, a pH of 8.9, a particle size of 291 nm and a Brookfield viscosity (#2, 60) of 143 cps.

[0045] The alkali-soluble resin used in Example 1 is designated as ASR A and has the composition of 80 EA/20 MAA with 1.2% MMP. It was prepared as follows: A 3 liter glass reactor with an agitator, a thermocouple for monitoring the temperature and a reflux condenser, was charged with 625 g deionized water and 11 g of Polystep B-1 and purged with nitrogen. After heating to 85° C, 4.0 g of ammonium persulfate dissolved in 20 g of deionized water was added. A pre-emulsion prepared from 640 g ethyl acrylate, 160 g methacrylic acid, 9.6 g methyl mercaptopropionate, 16 g Polystep B-1 and 350 g deionized water and 1.0 g ammonium persulfate dissolved in 90 g of deionized water were added uniformly over 3 hours while maintaining the temperature at 85° C. When the additions were complete, the reactor was held at 85° C for an additional 30 minutes. The reactor was then cooled to 60° C and 1 g t-butyl hydroperoxide dissolved in 5 g of deionized water and 0.7 g of sodium formaldehydesulfoxylate dissolved in 10 g of deionized water were added. The resulting alkali-soluble resin had a solids content of 42.0 %, a pH of 2.2, a particle size of 156 and a Brookfield viscosity (#1, 60) of 13 cps and a weight average molecular weight of 17000.

[0046] The aminosilane used in this example is A0742 manufactured by Huls. Chemically, A0742 is 3-aminopropyl-methyldiethoxy silane. In this example, 10 weight percent of ASR A was added to 90 weight percent of Latex A and then under agitation, the appropriate amount of aminosilane (A0742) was added to neutralize all of the acid in ASR A. In this example, it required 4.89kg (10.8 lbs) of A0742 per 0.3785m³ (100 gallon) paint formulation. The blend was added to the paint as the latex following normal paint making protocol known to those skilled in the art. The specific paint formulation used in Example 1 is as follows:

Material Name		Kg (Pounds)	
<u>M³x10⁻³</u>		<u>Gallons</u>	
5	Natrosol 250 MHR (2.5%)	54.43 (120.0)	54.50
	(14.40)		
	Water		9.07 (20.0)
	9.08	(2.40)	
	Propylene Glycol	27.21	(60.0)
10	26.23	(6.93)	
	Tamol 165		9.29 (20.5)
	8.78	(2.32)	
	Triton CF-10	0.45	(1.0)
	0.41	(0.11)	
15	Colloid 643		0.90 (2.0)
	0.98	(0.26)	
	Kathon LX (1.5%)	0.81	(1.8)
	0.83	(0.22)	
	Ti-Pure R-902	102.06	(225.0)
20	25.54	(6.75)	
	Icecap K		22.68 (50.0)
	8.62	(2.28)	
	Minex 4		70.58 (155.6)
	27.13	(7.17)	
25	<i>Grind the above on a high speed impeller mill at 3800-4500 FPM for 20 minutes. At a slower speed, let down as follows:</i>		
	{Latex A (54.7% solids)	140.84 (310.5)	131.60
	(34.77)		
30	Blend {ASR A (41.9% solids)	20.41	(45.0)
	19.03 (5.03)		
	{Aminosilane A0742 (100%)	4.89 (10.8)	5.29
	(1.40)		
	Texanol 4.26	(9.4)	4.50 (1.19)
35	Colloid 643 0.90	(2.0)	0.98 (0.26)
	Natrosol 250 MHR (2.5%)	22.86 (50.4)	22.08
	(6.05)		
	Water 31.97	(70.5)	32.0 (8.46)
	Totals		523.68 (1154.5)
40	378.5	(100.00)	

TABLE I

Latex	ASR	Amine	Crosshatch Knife Peel Force-to-Peel		
Substrate=Chalky Alkyd					
Latex A	none	NH ₄ OH	5	5	700 - Ad/Co
Latex A	10% ASR A	A0742	100	8	1450 - Co
Latex A = Latex with composition equal to 49 BA/ 49 MMA/ 2 MAA, particle size = 291 nm. ASR A = 80 EA/ 20 MAA with 1.2% MMP as chain transfer agent, particle size = 156 nm. A0742 is aminosilane: 3-aminopropylmethyldiethoxy silane.					

Example 2

[0047] Example 2 demonstrates that improvements in chalk adhesion are obtained by blending both the alkali-soluble resin and the aminosilane with a macromolecular aqueous dispersion. Blending of either the alkali-soluble resin or the aminosilane with the macromolecular aqueous dispersion without the other does not provide for significant improvements in chalk adhesion. The macromolecular aqueous dispersion in this example is designated as Latex B. Latex B was prepared according to the procedure for Latex A except that the pre-emulsion contained 980 g of styrene in place of the 980 g of methyl methacrylate. The resulting latex had a solids content of 54.6%, a pH of 8.8, a particle size of 297 nm and a Brookfield viscosity (#2, 60) of 98 cps.

[0048] The blend of Latex B with ASR A and aminosilane A0742 was added to the same paint formulation as in Example 1.

TABLE II

Latex	ASR	Amine	CrosshatchKnife PeelForce-to-Peel		
Substrate=Chalky Alkyd					
Latex B	none	NH ₄ OH	0	1+	400 - Ad
Latex B	10% ASR A	NH ₄ OH	17	1	150 - Ad
Latex B	none	A0742	0	1+	250 - Ad
Latex B	10% ASR A	A0742	48	4	1650 - Co/S
Latex B = Latex with composition equal to 49 BA/ 49 Styrene/ 2 MAA, particle size = 297 nm. ASR A = 80 EA/ 20 MAA with 1.2% MMP as chain transfer agent, particle size = 156 nm. A0742 is aminosilane: 3-aminopropylmethyldiethoxy silane.					

Example 3

[0049] In Example 3 various changes in acid level, molecular weight, and composition of the alkali-soluble resin demonstrate consistent improvements in chalk adhesion. The alkali-soluble resins in this example are designated as ASR A, ASR B, ASR C, ASR D and ASR E. They are each blended with the macromolecular aqueous dispersion, Latex A, at 10 weight percent. ASR B with a composition of 90 EA/10 MAA with 1.2 % MMP was prepared according to the Procedure for ASR A, except that 720 g of EA and 80 g of MAA were used to prepare the pre-emulsion. The resulting ASR had a solids content of 41.8 %, a pH of 2.0, a particle size of 137 nm, a Brookfield viscosity (#1, 60) of 11 cps and a weight average molecular weight of 15,500. ASR C with a composition of 70 EA/30 MAA with 1.2 % MMP was prepared according to the procedure for ASR A, except that 560 g of EA and 240 g of MAA were used to prepare the pre-emulsion. The resulting ASR had a solids content of 42.1 %, a pH of 2.1, a particle size of 292 nm, a Brookfield viscosity (#1, 60) of 10 cps and a weight average molecular weight of 17,000. ASR D with a composition of 70 EA/30 MAA with 1.2 % MMP is similar to ASR A but with a lower molecular weight and was prepared according to the procedure for ASR A, except that 19.2 g of MMP was used to prepare the pre-emulsion. The resulting ASR had a solids content of 42.2 %, a pH of 2.1, a particle size of 195 nm, a Brookfield viscosity (#1, 60) of 12 cps and a weight average molecular weight of 8,500. ASR E with a composition of 33.3 BA/9.5 STY/33.3 MMA/23.9 MAA with 1.1 % MMP was prepared according to the procedure for ASR A, except that 280 g BA, 280 g MMA, 80 g STY, 200 g of MAA and 9.6 g of MMP were used to prepare the pre-emulsion. The resulting ASR had a solids content of 42.5 %, a pH of 2.4, a particle size of 79 nm and a Brookfield viscosity (#1, 60) of 34 cps.

[0050] The blends in this example were formulated into the same paint formulation as Example 1.

TABLE III

Latex	ASR	Amine	CrosshatchKnife PeelForce-to-Peel		
Substrate=Chalky Alkyd					
Latex A	none	NH ₄ OH	0	4	650 - Ad/Co
Latex A	10% ASR B	A0742	31	7	1700 - Co/Ad

TABLE III (continued)

Latex	ASR	Amine	CrosshatchKnife PeelForce-to-Peel		
Latex A	10% ASR A	A0742	100	7	1450 - Co
Latex A	10% ASR C	A0742	100	8	1400 - Co
Latex A	10% ASR D	A0742	100	8	1300 - Co/S
Latex A	10% ASR E	A0742	100	5	1700 - Co/S
Latex A = Latex with composition equal to 49 BA/ 49 MMA/ 2 MAA, particle size = 291 nm. ASR A = 80 EA/ 20 MAA with 1.2% MMP as chain transfer agent, particle size = 156 nm. ASR B = 90 EA/ 10 MAA with 1.2% MMP as chain transfer agent, particle size = 137 nm. ASR C = 70 EA/ 30 MAA with 1.2% MMP as chain transfer agent, particle size = 292 nm. ASR D = 80 EA/ 20 MAA with 2.4% MMP as chain transfer agent, particle size = 195 nm. ASR E = 33.5BA/9.5 STY/33.3MMA/23.9MAA with 1.1% MMP as chain transfer agent, particle size = 79 nm. A0742 is aminosilane: 3-aminopropylmethyldiethoxy silane.					

Example 4

[0051] In this example, the adhesion to chalky substrates is demonstrated with blends of an acid-functional alkali-soluble resin and aminosilane with various macromolecular aqueous dispersions with different compositions. In this example, Latex C has the composition of 79.5 VA/20 BA/ 0.5 SVS and was prepared by the following procedure: A 5 liter glass reactor equipped with an agitator, a thermocouple for monitoring the temperature and a reflux condenser, was charged with 800 g of deionized water and purged with nitrogen. After heating to 80° C, 4.0 g of ammonium persulfate dissolved in 20 g of deionized water and 165 g of a seed latex (45% solids, 100 nm diameter) were added to the reactor. The temperature was adjusted to 76° C, and then a pre-emulsion prepared from 1590 g vinyl acetate, 400 g butyl acrylate, 40 g of sodium vinylsulfonate (25% ai), 5 g of sodium dodecylbenzenesulfonate, 57.4 g Triton X-405 and 517 g deionized water and an additional 3.0 g of ammonium persulfate dissolved in 90 g deionized water were added to the reactor over a three hour time period while maintaining the temperature at 76° C. When the additions were complete, the temperature was maintained at 76° C for an additional 30 minutes. The reaction was cooled to 70° C and 4 g of t-butyl hydroperoxide dissolved in 50 g of deionized water and 3.5 g of sodium formaldehydesulfoxylate dissolved in 50 g of deionized water were added. The pH was adjusted with 2 g of NaOH dissolved in 22 g deionized water. The resulting latex had a solids content of 54.7%, a pH of 5.5, a particle size of 265 nm and a Brookfield viscosity (#1, 60) of 48 cps.

[0052] The macromolecular aqueous dispersions in this example are designated as Latex A, Latex B and Latex C. ASR A at 10 weight percent is added to each macromolecular aqueous dispersion and then neutralized with A0742, the aminosilane. These blends were then added to the same paint formulation as in Example 1. This example also demonstrates the performance of the invention over chalky substrates which have varying degrees of severity due to differences in natural weathering conditions (Board #1 versus Board #2).

TABLE IV

Latex	ASR	Amine	CrosshatchKnife PeelForce-to-Peel		
Substrate=Chalky Alkyd , Board #1					
Latex A	none	NH ₄ OH	0	1+	200 - Ad
Latex A	10% ASR A	A0742	0	4	1350 - Co/S
Latex B	none	NH ₄ OH	0	1+	400 - Ad
Latex B	10% ASR A	A0742	48	4	1650 - Co/S
Latex C	none	NH ₄ OH	0	2	350 - Ad
Latex C	10% ASR A	A0742	43	4	1250 - Co
Substrate=Chalky Alkyd, Board #2					
Latex A	none	NH ₄ OH	5	5	700 - Ad
Latex A	10% ASR A	A0742	100	8	1450 - Co/S

TABLE IV (continued)

Latex	ASR	Amine	Crosshatch	Knife Peel	Force-to-Peel
Latex B	none	NH ₄ OH	98	7	1050 - Ad/Co
Latex B	10% ASR A	A0742	100	9	1500 - Co/S
Latex C	none	NH ₄ OH	100	7	950 - Co/Ad
Latex C	10% ASR A	A0742	100	8	950 - Co/S
Latex A = Latex with composition equal to 49 BA/ 49MMA/ 2 MAA, particle size = 291 nm. Latex B = Latex with composition equal to 49 BA/ 49 Styrene/ 2 MAA, particle size = 297 nm. Latex C = Latex with composition equal to 79.5 VA/20 BA/0.5 SVS, particle size = 265 nm. ASR A = 80 EA/ 20 MAA with 1.2% MMP as chain transfer agent, particle size = 156 nm.					

Example 5

[0053] In Example 5, the alkali-soluble resin, ASR A, is blended with a commercial macromolecular aqueous dispersion at levels from 6 weight percent to 10 weight percent. The resulting blends were then neutralized to varying degrees, 60% to 100%, with the aminosilane A0742. Improvements in adhesion to chalky substrates were realized at various levels of alkalisoluble resin and percent neutralization with aminosilane. The paint formulation in this example is the same as in Example 1.

TABLE V

Latex	ASR Level	% Neutralization with A0742	Crosshatch	Knife Peel	Force-to-Peel
Substrate = Latex D	Chalky Alkyd				
Latex D	0%	0%	0	5	100 - Ad
Latex D	6%	60%	0	3+	1050 - Co/Ad
Latex D	6%	80%	0	4	1050 - Co/Ad
Latex D	6%	100%	0	4	1200 - Co/Ad/S
Latex D	6%	120%	2	6	1700 - Co/S
Latex D	8%	60%	0	6	1450 - Co/Ad
Latex D	8%	80%	0	6	1700 - Co
Latex D	8%	100%	4	7	1700 - Co
Latex D	8%	120%	90	8	1450 - Co/S
Latex D	10%	60%	1	7+	500 - Ad/Co
Latex D	10%	80%	13	8+	1250 - Co/S
Latex D	10%	100%	92	8+	1250 - Co/S
Latex D	10%	120%	98	8+	1350 - Co/S

Latex D= Rhoplex AC-388, a commercial latex available from Rohm and Haas Company.

ASR = ASR A = 80 EA / 20 MAA

Aminosilane used in this case is 3-aminopropylmethyldiethoxy silane.

Claims

1. Use in water based latex paint, comprising a macromolecular dispersion (a), of an acid-functional alkali-soluble resin (b) having an acid level from 5 to 50 weight percent, based on the weight of the alkali-soluble resin, and a weight average molecular weight of less than 100,000; and an aminosilane (c) at a level to neutralize from 50 to 120 percent on the acid functionality of the alkali-soluble resin; for improving adhesion of the paint to chalky substrates.
2. Use as claimed in claim 1, wherein the macromolecular dispersion is present in the paint at levels from 50 weight percent to 99 weight percent based of a), b) and c).
3. Use as claimed in claims 1 or 2, wherein the acid level of the acid-functional alkali-soluble polymer is from 10 to 30 weight percent based on the weight of the alkali-soluble resin.
4. Use as claimed in any one of the preceding claims, wherein the aminosilane is added to the paint at a level to neutralize from 60 to 100 percent of the acid-functionality of the alkali-soluble resin.
5. Use as claimed in any one of the preceding claims, wherein the aminosilane is selected from the group consisting of trimethoxysilylpropyldiethylenetriamine, N-methylaminopropyltrimethoxysilane, N-(2-aminoethyl)-3-aminopropylmethyldimethoxysilane, N-(2-aminoethyl)-3-aminopropyltrimethoxysilane, aminopropylmethyldimethoxysilane, 3-aminopropyltrimethoxysilane, 3-aminopropylmethyldiethoxysilane, and methylaminopropyltriethoxysilane.
6. Use as claimed in any one of claims 1-5 wherein the paint is an exterior latex paint.
7. A composition for use in or as a water based latex paint having improved adhesion to chalky substrate, which composition consists essentially of (a) a macromolecular aqueous dispersion (b) 5 to 20 weight percent based on the total weight of said macromolecular aqueous dispersion of an acid-functional alkali-soluble resin polymerized from monomers selected from the group consisting of olefinically unsaturated compounds, vinyl esters and monovinyl aromatic compounds, said resin having a weight average molecular weight of less than 100,000 and having an acid level of from 5 to 50 weight percent, based on the weight of the alkali-soluble resin; and (c) an aminosilane selected from the group consisting of trimethoxysilylpropyldiethylenetriamine, N-methylaminopropyltrimethoxysilane, N-(2-aminoethyl)-3-aminopropylmethyldimethoxysilane, N-(2-aminoethyl)-3-aminopropyltrimethoxysilane, aminopropylmethyldimethoxysilane, 3-aminopropyltrimethoxysilane, 3-aminopropylmethyldiethoxysilane, and 3-aminopropyltriethoxysilane, at a level to neutralize from 50 to 120 percent on the acid functionality of the alkali-soluble resin.
8. The composition of claim 7, where the macromolecular aqueous dispersion is present in the blend at levels from 50 weight percent to 99 weight percent based on the weight of the total polymer.
9. The composition of claim 7 or claim 8, wherein the macromolecular aqueous dispersion has a particle size in the range of from 0.05 to 1.0 micron.

Patentansprüche

1. Verwendung in Latexfarbe auf Wasserbasis, umfassend eine makromolekulare Dispersion (a) eines säurefunktionalen Alkali-löslichen Harzes (b) mit einem Säuregrad von 5 bis 50 Gewichtsprozent, bezogen auf das Gewicht des Alkali-löslichen Harzes, und einem durchschnittlichen Molekulargewicht von weniger als 100.000 und ein Aminosilan (c) in einer Konzentration, um von 50 bis 120 Prozent der Säurefunktionalität des Alkali-löslichen Harzes zu

neutralisieren, zur Erhöhung der Haftung der Farbe auf kalkigen Substraten.

2. Verwendung gemäß Anspruch 1, worin die makromolekulare Dispersion in der Farbe in Konzentrationen von 50 Gewichtsprozent bis 99 Gewichtsprozent, bezogen auf a), b) und c), anwesend ist.

3. Verwendung gemäß Anspruch 1 oder 2, worin der Säuregehalt des säurefunktionalen Alkali-löslichen Polymers von 10 bis 30 Gewichtsprozent, bezogen auf das Gewicht des Alkali-löslichen Harzes, beträgt.

4. Verwendung gemäß einem der vorangehenden Ansprüche, worin das Aminosilan zu der Farbe in einer Konzentration hinzugegeben wird, um von 60 bis 100 Prozent der Säurefunktionalität des Alkali-löslichen Harzes zu neutralisieren.

5. Verwendung gemäß einem der vorangehenden Ansprüche, worin das Aminosilan ausgewählt wird aus der Gruppe, bestehend aus Trimethoxysilylpropyldiethylentriamin, N-methylaminopropyltrimethoxysilan, N-(2-aminoethyl)-3-aminopropylmethyldimethoxysilan, N-(2-aminoethyl)-3-aminopropyltrimethoxysilan, Aminopropylmethyldimethoxysilan, 3-Aminopropyltrimethoxysilan, 3-Aminopropylmethyldiethoxysilan, und Methylaminopropyltriethoxysilan.

6. Verwendung gemäß einem der Ansprüche 1 - 5, worin die Farbe eine Außenanstrichlatexfarbe ist.

7. Eine Zusammensetzung für die Verwendung in einer oder als Latexfarbe auf Wasserbasis mit erhöhter Haftung auf kreidigem Substrat, wobei die Zusammensetzung im wesentlichen besteht aus (a) einer makromolekularen wässrigen Dispersion (b) 5 bis 20 Gewichtsprozent, bezogen auf das Gesamtgewicht der makromolekularen wässrigen Dispersion eines säurefunktionalen Alkali-löslichen Harzes, polymerisiert aus Monomeren, ausgewählt aus der Gruppe, bestehend aus olefinisch ungesättigten Verbindungen, Vinylestern und Monovinyl-, aromatischen Verbindungen, wobei das Harz ein durchschnittliches Molekulargewicht von weniger als 100.000 und einen Säuregrad von 5 bis 50 Gewichtsprozent, bezogen auf das Gewicht des Alkali-löslichen Harzes, aufweist und (c) einem Aminosilan, ausgewählt aus der Gruppe, bestehend aus Trimethoxysilylpropyldiethylentriamin, N-methylaminopropyltrimethoxysilan, N-(2-aminoethyl)-3-aminopropylmethyldimethoxysilan, N-(2-aminoethyl)-3-aminopropyltrimethoxysilan, Aminopropylmethyldimethoxysilan, 3-Aminopropyltrimethoxysilan, 3-Aminopropylmethyldiethoxysilan und 3-Aminopropyltriethoxysilan, in einer Konzentration, um von 50 bis 120 Prozent der Säurefunktionalität des Alkali-löslichen Harzes zu neutralisieren.

8. Die Zusammensetzung nach Anspruch 7, worin die makromolekulare wässrige Dispersion in der Mischung in Konzentrationen von 50 Gewichtsprozent bis 99 Gewichtsprozent, bezogen auf das Gewicht des Gesamtpolymers, anwesend ist.

9. Die Zusammensetzung nach Anspruch 7 oder Anspruch 8, worin die makromolekulare wässrige Dispersion eine Partikelgröße im Bereich von 0,05 bis 1,0 Mikrometer hat.

Revendications

1. Utilisation, dans une peinture de latex aqueuse comprenant une dispersion macromoléculaire (a), d'une résine à fonctionnalité acide soluble dans une base (b) ayant une teneur en acide de 5 à 50 % en poids, par rapport au poids de la résine soluble dans une base, et un poids moléculaire moyen en poids inférieur à 100 000 ; et d'un aminosilane (c) à une concentration qui neutralise de 50 à 120 % de la fonctionnalité acide de la résine soluble dans une base ; pour améliorer l'adhésion de la peinture à des substrats crayeux.

2. Utilisation selon la revendication 1, dans laquelle la dispersion macromoléculaire est présente dans la peinture à des concentrations de 50 à 99 % en poids par rapport à a), b) et c).

3. Utilisation selon les revendications 1 ou 2, dans laquelle la teneur en acide du polymère à fonctionnalité acide soluble dans une base est de 10 à 30 % en poids par rapport au poids de la résine soluble dans une base.

4. Utilisation selon l'une quelconque des revendications précédentes, dans laquelle l'aminosilane est ajouté à la peinture en une concentration qui neutralise de 60 à 100 % de la fonctionnalité acide de la résine soluble dans une base.

5. Utilisation selon l'une quelconque des revendications précédentes, dans laquelle l'aminosilane est choisi dans le groupe constitué par une triméthoxysilylpropyldiéthylènetriamine, un N-méthylaminopropyltriméthoxysilane, un N-(2-aminoéthyl)-3-aminopropylméthyltriméthoxysilane, un N-(2-aminoéthyl)-3-aminopropyltriméthoxysilane, un aminopropylméthyltriméthoxysilane, un 3-aminopropyltriméthoxysilane, un 3-aminopropylméthyltriéthoxysilane et un méthylaminopropyltriéthoxysilane.
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6. Utilisation selon l'une quelconque des revendications 1 à 5, dans laquelle la peinture est une peinture au latex d'extérieur.
- 10 7. Composition pour l'utilisation dans ou sous la forme d'une peinture au latex aqueuse ayant une adhésion améliorée à un substrat crayeux, cette composition étant essentiellement constituée par (a) une dispersion aqueuse macromoléculaire, (b) 5 à 20 % en poids, par rapport au poids total de ladite dispersion aqueuse macromoléculaire, d'une résine à fonctionnalité acide soluble dans une base, polymérisée à partir de monomères choisis dans le groupe
15 constitué par les composés oléfiniquement insaturés, les esters vinyliques et les composés aromatiques monovinyls, ladite résine ayant un poids moléculaire moyen en poids inférieur à 100 000 et ayant une teneur en acide de 5 à 50 % en poids, par rapport au poids de la résine soluble dans une base ; et (c) un aminosilane choisi dans le groupe constitué par une triméthoxysilylpropyldiéthylènetriamine, un N-méthylaminopropyltriméthoxysilane, un N-(2-aminoéthyl)-3-aminopropylméthyltriméthoxysilane, un N-(2-aminoéthyl)-3-aminopropyltriméthoxysilane, un aminopropylméthyltriméthoxysilane, un 3-aminopropyltriméthoxysilane, un 3-aminopropylméthyltriéthoxysilane et
20 un 3-aminopropyltriéthoxysilane, à une concentration qui neutralise de 50 à 120 % de la fonctionnalité acide de la résine soluble dans une base.
8. Composition selon la revendication 7, dans laquelle la dispersion aqueuse macromoléculaire est présente dans le mélange à des concentrations de 50 % en poids à 99 % en poids par rapport au poids du polymère total.
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9. Composition selon la revendication 7 ou la revendication 8, dans laquelle la dispersion aqueuse macromoléculaire a une taille de particule dans la gamme de 0,05 à 1,0 μm .

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